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The Molecular Configuration of the Decaniobate Ion ($Nb_{10}O_{28}^{6-}$)*

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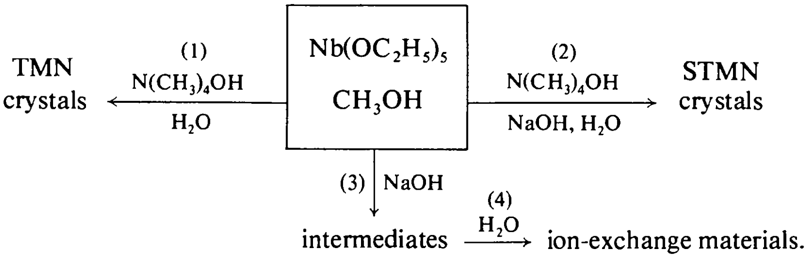
The molecular configuration of the decaniobate ion ($Nb_{10}O_{28}^{6-}$) has been found by the determination of two crystal structures, $[N(CH_3)_4]_4Na_2Nb_{10}O_{28}.8H_2O.\frac{1}{2}CH_3OH$ and $[N(CH_3)_4]_6Nb_{10}O_{28}.6H_2O$. The octahydrate compound is monoclinic, space group $I2/m$, with cell dimensions $a = 12·056\,(7)$, $b = 20·501\,(8)$, $c = 10·980\,(7)$ Å, $\beta = 90·05\,(4)°$ ($Z = 2$); the hexahydrate crystallizes in $P2_1/n$, with $a = 14·534\,(8)$, $b = 18·668\,(6)$, $c = 10·990\,(7)$ Å, $\beta = 92·50\,(4)°$ ($Z = 2$). Unique data sets of 4105/2156 reflections for the hexahydrate/octahydrate were collected by the θ–2θ scan technique; both structures were determined from Patterson and Fourier syntheses and refined by least-squares methods to $R = 4\%$. The decaniobate ion is an isolated group of ten condensed NbO_6 octahedra. In the crystal structure, these ions are electrostatically linked by tetramethylammonium ions (and sodium ions) as well as by a hydrogen-bond network. Ten Nb atoms are situated on the corners of two edge-shared octahedra with 3·274–3·481 Å Nb–Nb separations; the 1·73–2·55 Å range of Nb–O separations indicates the distorted nature of the decaniobate ions.

Introduction

The alkoxides of Ti, Zr and Nb have been used as starting materials for the preparation of the perovskite class of ferroelectric and electrooptic ceramics (Dosch, 1971; Haertling & Land, 1972). Recently the same reaction scheme has been used to prepare a series of ion-exchange materials which Sandia Laboratories proposes to use to remove radio isotopes and stabilize radioactive wastes in the form of hot-pressed, essentially nonleachable, ceramic bodies. The ion-exchange materials typically yield X-ray diffraction patterns characteristic of amorphous materials and, hence, have required other experimental techniques for inference of their structural nature (Morosin & Peercy, 1976). The reaction scheme to produce Nb-based ion-exchange materials is the following:



In preparing these materials, pentaethyl niobate (PEN) (Research Organic/Inorganic Chemical Co., Sun Valley, California) and tetramethylammonium hydroxide (TMAOH) as a 20 w/o solution in methanol (Aldrich Chemical Co., Milwaukee, Wisconsin) were used without further purification. All other materials were AR grade or better. A typical preparation of TMN and STMN crystals (steps 1 and 2) was as follows. A mixture of 178·2 g PEN and 127·5 g TMAOH solution was diluted with 200 ml of methanol and 25 ml of water. One-half of this solution was covered and set aside (step 1). 5 ml of 15 w/o NaOH in methanol were added to the remaining half prior to covering. After 24 h, the crystalline materials which formed were removed, washed by decantation with ethanol, air-dried, and stored in closed containers.

Preparation of the ion-exchange materials involves reaction of PEN with NaOH dissolved in methanol (10–20 w/o), forming a soluble reaction product (step 3). Subsequent addition of this solution to water, or preferably acetone–water mixture (step 4), produces an amorphous solid, which, when dried, exhibits excellent ion-exchange properties.

The crystals of the tetramethylammonium complex, TMN, and the analogous sodium-containing material, STMN, are the only stable crystalline compounds obtained in the preparation of the ion-exchange materials to date. A few extremely unstable intermediate hydrol-

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ysis products have been obtained which almost instantly deteriorate upon removal from the mother solution. A wide variety of coating materials, including collodion, glues, waxes and fluorosilicones, were used to delay crystal deterioration sufficiently long for acquisition of X-ray data. The only partial success on such an intermediate involved a zirconium oxide methoxide complex (Morosin, 1977); however, to date, none of the ion-exchange materials have been crystallized. Consequently, the structures of the crystalline adjuncts (TMN and STMN) were determined so as to possibly provide some insight into the chemical behavior of the amorphous ion-exchange materials.

Experimental

Crystals of TMN and STMN were obtained from solution by controlled evaporation; both compounds had identical morphological characteristics (Fig. 1). The crystals used for the collection of X-ray data were approximately equi-dimensional and chosen with maximum dimensions not exceeding 0·37 mm, such that absorption corrections (for Mo $K\alpha$, $\mu = 18{\cdot}8$–$20{\cdot}4$ cm^{-1}) would be unnecessary.

Precession and Weissenberg photographs were used to determine preliminary unit-cell dimensions and space-group extinctions; such photographs were also necessary to inspect the diffraction images for satellites, since TMN usually exhibited twinning. Systematic absences and the symmetry of the reciprocal lattice indicated the space groups to be $P2_1/n$ and $I2/m$ for TMN and STMN respectively. The non-standard space group $I2/m$ was chosen, rather than a C-centered one, for convenience in making β close to 90°. Cell dimensions for both compounds were obtained from 19 reflections measured on a single-crystal diffractometer. Table 1 summarizes the crystallographic data for TMN and STMN. The calculated densities, based on the X-ray-determined cell contents, agree within less than a half of a percent with the observed densities as measured by suspension in carbon tetrachloride/tetrabromoethane mixtures. Table 2 lists the X-ray-determined compositions of STMN and TMN and the chemical analyses performed on a few of the remaining crystals. The agreement is quite good considering the small amounts of material analyzed.

The θ–2θ scan technique with a scintillation detector employing pulse-height discrimination was used to measure the Mo $K\alpha$ intensity data at room temperature. Reflections within a sphere limited by 2θ = 50° were measured with a β filter (Zr). Background radiation was measured at each end of the scan with crystal and counter stationary, and was assumed to be a linear function of 2θ between these points. Unique sets of 5229 and 2475 reflections were measured for TMN and STMN respectively; from these sets, 1124 and 319 reflections, respectively, were less than 3σ and hence considered unobserved. The value of σ is based on counting statistics, with $\sigma = \sqrt{(N_{sc} + K^2N_b)}$, where N_{sc}, N_b and K are the total scan counts, background counts and the time ratio of scan to background. Intensities were corrected for Lorentz and polarization effects to obtain the observed structure amplitudes; no corrections for absorption or extinction were applied.

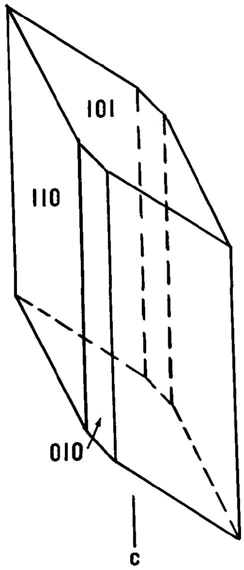

Fig. 1. Perspective drawing of TMN and STMN crystals.

Table 1. *Crystallographic data for TMN and STMN*

Standard errors are in parentheses.

	TMN	STMN
Space group	$P2_1/n$	$I2/m$
a (Å)	14·534 (8)	12·056 (7)
b	18·668 (6)	20·501 (8)
c	10·990 (7)	10·980 (7)
β (°)	92·50 (4)	90·05 (4)
Z	2	2
D_c (g cm^{-3})	2·15	2·27
D_o	2·16	2·26

Table 2. *Composition of STMN and TMN in wt %*

	STMN		TMN	
	X-ray	Chemical	X-ray	Chemical
Na	2·45	2·08		
Nb	49·42	49·50	48·14	48·10
O	31·07	31·30*	28·19	28·57*
N	2·98	2·83	4·35	4·18
C	10·54	11·16	14·94	14·76
H	3·54	3·49	4·39	4·39

* By difference.

Atomic scattering factors for Nb, Na, O, N and C were taken from Cromer & Mann (1968), and dispersion corrections from *International Tables for X-ray Crystallography* (1962).

Determination of the structures and refinement

Since the exact chemical formulae, molecular weights and cell contents were unknown for both compounds, the structures were deduced by utilizing phases based upon the location of heavy atoms in the Patterson syntheses. The least-squares procedure, together with analysis of Fourier syntheses, proceeded normally through the process of isotropic and anisotropic refinement. Both full-matrix and block least-squares routines were used throughout the refinements. The function $w(F_o - F_c)^2$ was minimized with $w = n/\sigma^2$; corrections for extinction were not included. The final residual indices, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, omitting 'less-thans', were 0·043/0·040 for 4105/2156 observed reflections for TMN/STMN respectively. The parameter shifts in the last cycle of refinement for both compounds were all less than two-tenths of the standard deviation. The final least-squares parameters are given in Table 3.* The values for the anisotropic thermal parameters for the tetramethylammonium ions in both compounds are large, as might be expected for such large weakly bonded ions. All numerical calculations were performed with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Results and discussion

Decaniobate ions

The two structures contain decaniobate ions, illustrated in Fig. 2, in which 10 Nb and 28 O atoms are arranged in a highly condensed system of NbO_6 octahedra. A group of six NbO_6 octahedra are arranged in a 2 × 3 rectangular array by sharing edges, with two NbO_6 octahedra joined above and two more below, again by sharing sloping edges with the other octahedra. Although other polyniobate complexes containing six and eight Nb atoms are known, this is the first reported polyniobate ion which contains ten condensed niobia octahedra. It is similar in configuration to several decavanadates (Evans, 1966; Swallow, Ahmed & Barnes, 1966; Safianov & Belov, 1976), but differs in an interesting way from a recently reported decatungstate, $W_{10}O_{32}^{4-}$ (Fuchs, Hartl, Schiller & Gerlach,

Table 3. *Final positional parameters* ($\times 10^5$ *for* Nb, $\times 10^4$ *for rest, except* $\times 10^3$ *for Me*)

E.s.d.'s of the refined parameters appear in parentheses.

	x	*y*	*z*
(*a*) TMN			
Nb(1)	5553 (6)	17678 (5)	−12711 (8)
Nb(2)	−669 (6)	17179 (5)	16499 (8)
Nb(3)	3210 (5)	231 (5)	−15060 (7)
Nb(4)	17201 (5)	7227 (5)	7777 (7)
Nb(5)	−14658 (5)	10265 (5)	−5745 (7)
O(1)	857 (5)	2442 (4)	−2269 (7)
O(2)	317 (5)	2271 (4)	250 (6)
O(3)	−181 (5)	2363 (4)	2788 (6)
O(4)	−801 (4)	1659 (4)	−1581 (6)
O(5)	−1311 (4)	1612 (4)	852 (6)
O(6)	1731 (4)	1410 (4)	−518 (6)
O(7)	1214 (4)	1367 (4)	1932 (5)
O(8)	630 (4)	841 (4)	−2322 (5)
O(9)	92 (4)	736 (3)	88 (5)
O(10)	−408 (4)	755 (4)	2499 (6)
O(11)	−2626 (4)	1142 (4)	−1069 (6)
O(12)	2860 (4)	621 (4)	1303 (6)
O(13)	1529 (4)	−109 (4)	−540 (5)
O(14)	1059 (4)	−143 (3)	1639 (5)
N(1)	3288 (6)	2997 (5)	375 (8)
N(11)	2308 (6)	1613 (5)	5039 (8)
N(21)	995 (6)	4517 (5)	−2953 (8)
C(1)	2849 (8)	2922 (8)	−874 (10)
C(2)	2567 (8)	2950 (7)	1342 (11)
C(3)	3825 (10)	3683 (7)	461 (11)
C(4)	3963 (9)	2383 (8)	586 (12)
C(11)	3023 (9)	1636 (7)	4055 (11)
C(12)	2814 (10)	1687 (8)	−3724 (10)
C(13)	1814 (9)	927 (7)	4950 (12)
C(14)	1663 (10)	2224 (7)	4871 (12)
C(21)	975 (13)	4670 (9)	−1619 (10)
C(22)	31 (10)	4306 (11)	−3387 (16)
C(23)	1333 (13)	5211 (9)	−3611 (17)
C(24)	1710 (10)	3955 (7)	−3195 (12)
W(1)	243 (8)	3745 (6)	794 (11)
W(2)	529 (6)	3707 (5)	3407 (10)
W(3)	1686 (9)	4835 (7)	1326 (11)
(*b*) STMN			
Nb(1)	3847 (10)	0	−15274 (10)
Nb(2)	3753 (8)	15968 (4)	−14797 (8)
Nb(3)	19036 (6)	8043 (4)	5962 (7)
Na	5000	915 (3)	0
O(1)	0	676 (4)	0
O(2)	0	2070 (4)	0
O(3)	1266 (7)	0	1583 (7)
O(4)	1206 (5)	1383 (3)	1706 (6)
O(5)	3282 (5)	806 (4)	1040 (6)
O(6)	−1840 (7)	0	630 (7)
O(7)	−1848 (5)	1384 (3)	776 (6)
O(8)	−616 (5)	726 (3)	2440 (5)
O(9)	−632 (6)	2193 (4)	2561 (7)
N(1)	2507 (8)	1606 (5)	4673 (8)
C(1)	1868 (13)	1001 (7)	4595 (13)
C(2)	1791 (17)	2177 (9)	4519 (17)
C(3)	3432 (14)	1600 (9)	3745 (13)
C(4)	3064 (14)	1636 (9)	5911 (12)
W(1)	4097 (14)	0	2907 (14)
W(2)	5819 (12)	0	1218 (13)
W(3)	5884 (7)	1578 (4)	1434 (8)
Me	566 (3)	0	470 (3)

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* Lists of structure factors, anisotropic thermal parameters, and bond lengths and angles for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32422 (91 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

1976), in which the W atoms of ten WO_6 octahedra form a bipyramid-capped cube. The Nb—O separations in Table 4 range between 1·73 and 2·55 Å, which gives an indication of the rather severe distortion in the NbO_6 octahedra in the polyion. The correspondence among Nb—O separations, for (1) unshared oxygens, (2) oxygens shared with two Nb atoms, (3) oxygens shared with three Nb atoms and (4) oxygens shared with six Nb atoms, is remarkable between the STMN and TMN structures. The distortions appear to be of the same magnitude and direction even in some of these subgroups (see Table 4, 'sharing six Nb atoms'). It should be noted that in STMN, the decaniobate ion is situated at a 2/*m* position, while in TMN it is at an inversion center only (see Figs. 4 and 5).

Within the decaniobate ion, 10 Nb atoms are situated at the corners of two edge-shared octahedra (see Fig. 3). The range of Nb—Nb separations (3·27–3·48 Å) again indicates the distortions within the decaniobate ion; again the two ions show similar trends

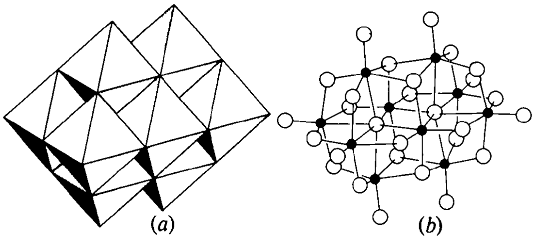

Fig. 2. Model structures of the $Nb_{10}O_{28}^{6-}$ group. (*a*) Polyhedral, and (*b*) bond models.

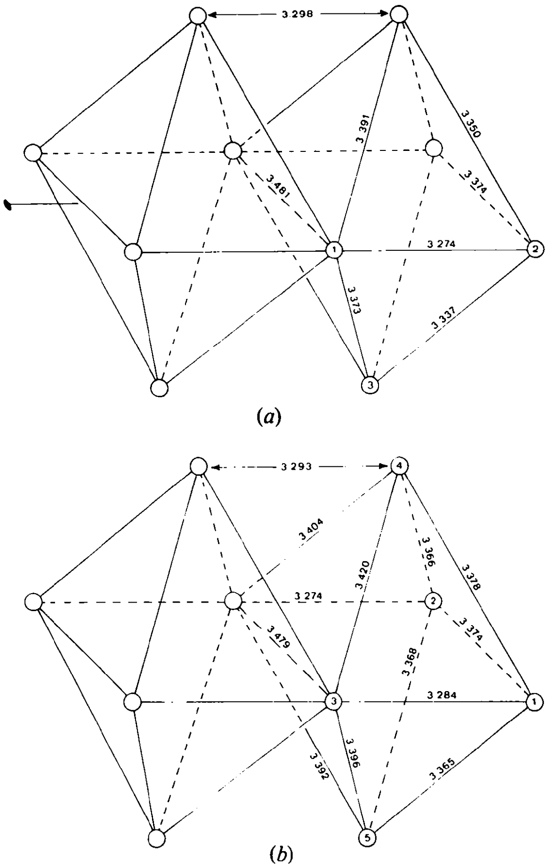

Fig. 3. Perspective view of Nb atoms in the decaniobate group for (*a*) STMN and (*b*) TMN; the e.s.d. for Nb—Nb distances is 0·002 Å.

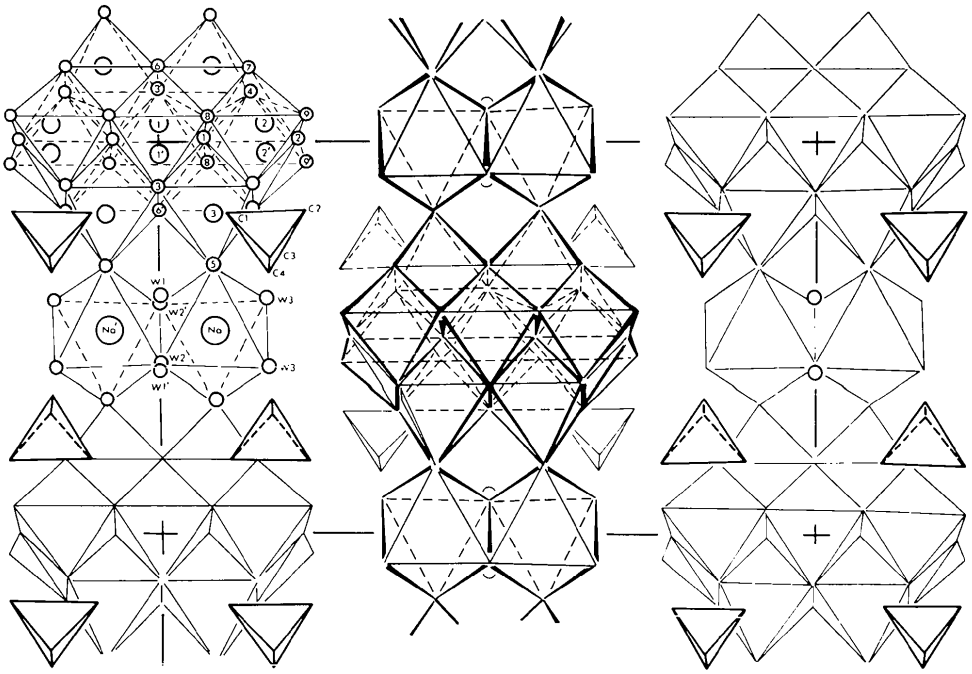

Fig. 4. Projection along [001] of the STMN unit cell; origin at upper left, z pointing out of the page.

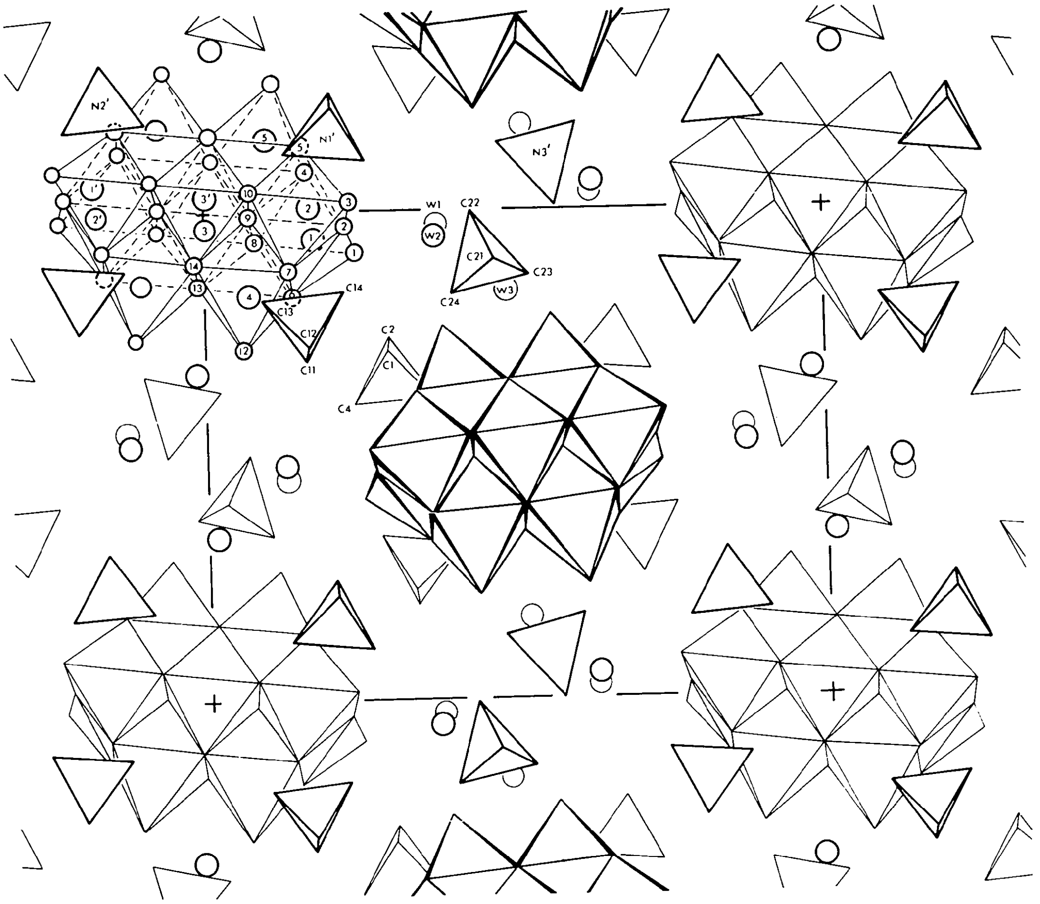

Fig. 5. Projection along [001] of the TMN unit cell; origin at upper left, z pointing out of the page.

in their octahedral distortions (*e.g.* the shared-edge Nb–Nb distance is the largest; that between the apexes, the smallest, *etc.*).

Sodium environment in STMN

The Na ion is situated on a twofold position (see Fig. 4). The coordination sphere consists of two O atoms on two different decaniobate ions [O(5)] and four water molecules, *W*(2) and *W*(3); the arrangement is distorted octahedral with bond distances ranging between 2·34 and 2·51 Å; the O–Na–O angles range between 81 and 109°, and 167 and 169°. The Na ion links the decaniobate ions along **a**.

Hydrogen bonding

In both structures, a hydrogen-bonding network links the decaniobate ions (together with the electrostatic forces of the tetramethylammonium and, for STMN, Na ions). In STMN, the hydrogen bonding of *W*(1) bridges two symmetry-related O atoms [O(5)] on the same decaniobate ion at an unusually small angle of 72° (see Fig. 6). *W*(2) is part of the Na environment

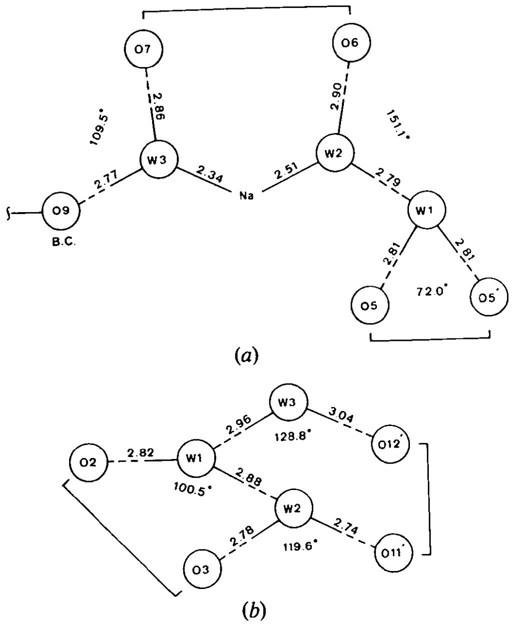

Fig. 6. Hydrogen bonding for (*a*) STMN and (*b*) TMN; e.s.d.'s for Na–O and O–O distances and angles are 0·01 Å, 0·02 Å and 0·7° respectively.

Table 4. *Bond lengths* (Å) *with standard deviations for STMN and TMN*

×*n* refers to *n* equivalent distances.

STMN			TMN		
Unshared oxygens					
Nb(2)–O(9)	1·733 (7)	×4	Nb(1)–O(1)	1·738 (9)	×2
			Nb(2)–O(3)	1·750 (8)	×2
Nb(3)–O(5)	1·731 (6)	×4	Nb(5)–O(11)	1·763 (7)	×2
			Nb(4)–O(12)	1·741 (7)	
Oxygens sharing two Nb atoms					
Nb(1)–O(8)	1·816 (7)	×4	Nb(3)–O(8)	1·836 (8)	×2
			Nb(3)–O(10)	1·824 (8)	×2
Nb(2)–O(2)	1·946 (4)	×4	Nb(1)–O(2)	1·961 (8)	×2
			Nb(2)–O(2)	1·954 (8)	×2
Nb(2)–O(4)	1·972 (6)	×4	Nb(1)–O(6)	1·982 (7)	×2
			Nb(2)–O(7)	1·985 (7)	×2
Nb(2)–O(8)	2·094 (7)	×4	Nb(1)–O(8)	2·086 (8)	×2
			Nb(2)–O(10)	2·095 (8)	×2
Nb(2)–O(7)	1·984 (6)	×4	Nb(1)–O(4)	1·995 (7)	×2
			Nb(2)–O(5)	1·985 (7)	×2
Nb(3)–O(4)	1·898 (6)	×4	Nb(4)–O(6)	1·918 (8)	×2
			Nb(5)–O(5)	1·916 (8)	×2
Nb(3)–O(7)	1·920 (7)	×4	Nb(4)–O(7)	1·917 (7)	×2
			Nb(5)–O(4)	1·910 (8)	×2
Oxygens sharing three Nb atoms					
Nb(1)–O(3)	1·991 (8)	×2	Nb(3)–O(13)	2·027 (7)	×2
Nb(1)–O(6)	2·011 (9)	×2	Nb(3)–O(14)	2·016 (7)	×2
Nb(3)–O(3)	2·118 (5)	×4	Nb(4)–O(13)	2·133 (7)	×2
			Nb(5)–O(13)	2·110 (7)	×2
Nb(3)–O(6)	2·130 (5)	×4	Nb(4)–O(14)	2·124 (7)	×2
			Nb(5)–O(14)	2·122 (7)	×2
Oxygens sharing six Nb atoms					
Nb(1)–O(1)	2·225 (5)	×4	Nb(3)–O(9)	2·209 (7)	×2
			Nb(3)–O(9)	2·237 (7)	×2
Nb(2)–O(1)	2·531 (6)	×4	Nb(1)–O(9)	2·546 (7)	×2
			Nb(2)–O(9)	2·528 (7)	×2
Nb(3)–O(1)	2·400 (1)	×4	Nb(4)–O(9)	2·453 (7)	×2
			Nb(5)–O(9)	2·410 (7)	×2
⟨N–C⟩	1·49 (2)	×4	⟨N–C⟩	1·51 (2)	×12
Na–O(5)	2·377 (9)	×2			
Na–*W*(2)	2·505 (10)	×2			
Na–*W*(3)	2·337 (9)	×2			

and bonds to *W*(1) as well as to an O atom [O(6)] of another decaniobate ion a lattice translation away along **c**. *W*(3) is also part of the Na environment and bonds to O(7) of this same decaniobate ion as well as to a different O atom [O(9)] belonging to the body-centered decaniobate ion. In TMN, the hydrogen bonding of *W*(2) bridges two O atoms [O(11)′ and O(3)] on different decaniobate ions; *W*(1) bonds to *W*(2) and O(2) of one of the previous decaniobate ions. *W*(3) bridges *W*(1) and O(12)′ of the other decaniobate ion.

Disorder in STMN

In the case of STMN, a difference Fourier synthesis indicated positive electron density inside a hole in the structure at a 2/*m* symmetry site ($\frac{1}{2}$,0,$\frac{1}{2}$); this density consisted of two peaks separated by ~1·5 Å with the nearest neighbors to these peaks being at distances greater than 3 Å. This hole appears to be occupied by a disordered methyl alcohol molecule (Me in Table 3). The refined position corresponds to a 1·72 (5) Å C–O length; such a long distance appears acceptable within the approximation of our model (no H atoms included; disorder).

Relation to ion-exchange materials

In a complementary study (Morosin & Peercy, 1976), Raman scattering was employed to identify the vibrational modes of the amorphous Na ion-exchange materials, for these two compounds and the corresponding sintered materials. These results suggested that the structure of the niobate units in the amorphous material have a form similar to those of the sintered materials, rather than similar to the $Nb_{10}O_{28}^{6-}$ ion. The sintered material corresponds to a mixture of $Na_{13}Nb_{35}O_{94}$ and $Na_2Nb_4O_{11}$. The structure of $Na_{13}Nb_{35}O_{94}$ consists primarily of *corner*-shared niobia octahedra with additional Nb ions in edge-shared pentagonal bipyramids; that of $Na_2Nb_4O_{11}$ consists of alternate, fused layers of edge-shared pentagonal bipyramids and isolated niobia octahedra edge-shared with Na octahedra. Such continuously linked niobia polyhedra are to be contrasted with the discrete decaniobate ion ($Nb_{10}O_{28}^{6-}$) units comprised of 10 edge-shared niobia octahedra, which occur in these crystalline tetramethylammonium (TMN and STMN) compounds.

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The Crystal and Molecular Structure of (±)-Octopamine Hydrochloride

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The hydrochloride of octopamine [α-(aminomethyl)-p-hydroxybenzyl alcohol] crystallizes in the monoclinic space group $P2_1/c$ with $a = 10{\cdot}73\,(1)$, $b = 8{\cdot}50\,(1)$, $c = 10{\cdot}58\,(1)$ Å, $\beta = 106{\cdot}1\,(1)°$, $Z = 4$. The structure was refined by least squares to R 7·6% for 416 observed counter amplitudes. Estimated standard deviations for bond lengths, bond angles and torsion angles average 0·02 Å, 1·5 and 2·0°. The ethanolamine side chain is in the extended conformation, the C—C—C—N$^+$ torsion angle being 171°. The best plane through these atoms makes an angle of 79° with the plane of the phenyl ring.

Introduction

Octopamine, α-(aminomethyl)-p-hydroxybenzyl alcohol, a biogenic amine closely related to noradrenaline was first discovered in the posterior salivary gland of the octopus (Erspamer, 1952) and was subsequently identified in urine from several mammalian species (Kakimoto & Armstrong, 1962). More recently, octopamine has been found in sympathetically innervated mammalian organs (Molinoff & Axelrod, 1969), in a number of other molluscs (Juorio & Molinoff, 1974; Saavedra, Brownstein, Carpenter & Axelrod, 1974; Roseghini & Alcala, 1976), and in the insect nervous system (Robertson, 1976; Robertson & Carlson, 1976). In anaesthetized dogs and cats it produces sympathomimetic cardiovascular effects, although it is markedly less potent than noradrenaline (Kappe & Armstrong, 1964). The physiological role of octopamine is not known with certainty, but it has been suggested (Saavedra *et al.*, 1974; Robertson & Carlson, 1976) that in invertebrate nervous systems it may act as a neurotransmitter.

We now report the crystal structure analysis of (±)-octopamine hydrochloride. It was hoped that by comparing its structure with those of the sympathomimetic catecholamines, whose structures have previously been determined (Carlström, Bergin & Falkenberg, 1973; Giesecke, 1976), a stereochemical basis for the differences in biological function might be obtained. The results of the present analysis, however, show that in the solid state, octopamine adopts a conformation which is virtually identical to that found for noradrenaline (Carlström & Bergin, 1967). Most of the related catecholamines whose structures are known also adopt similar conformations (Carlström *et al.*, 1973).

Experimental

Crystals suitable for X-ray analysis were kindly supplied by Dr R. A. Thornhill of the Department of Zoology, Birmingham University. After initial examination by photographic methods final cell dimensions and intensities were measured on a Stoe two-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The crystal, 0·5 × 0·15 × 0·05 mm, was mounted about the direction of elongation (**c**). With the diffractometer operating in the ω-scan mode, 140 counts of 1 s at intervals of 0·01° were taken for each reflexion on layers 0–2. For reflexions on the third and higher layers, the peak scan was defined by the expression $(A + B \sin \mu/\tan \theta')°$ where μ is the equi-inclination angle and θ' is half the azimuth angle. The constants A and B were assigned the values 1·2 and 0·5°, respectively. Backgrounds were measured for 30 s at each end of the scan. Reflexions were scanned within the range $0{\cdot}1 < \sin \theta/\lambda < 0{\cdot}54$ and, of these, 416 [$I > 2{\cdot}5\sigma(I)$] were considered observed and used in the structure analysis. In the conversion of intensities to structure amplitudes, the polarization factor appropriate to monochromated radiation was used. Absorption corrections were not applied.